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THE KINETICS OF THE OXIDATION OF PROPANE
CATALYZED WITH HYDROGEN BROMIDE

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The action of homogeneous and heterogeneous catalysts in various reactions belongs to the oldest and best known chemical phenomena. However, the extent of research done on these two types of catalysts is not on the same level. Heterogeneous catalysts are used on a wide scale in chemical practice, and for that reason intensive research is being carried out in the field of heterogeneous catalysis. Homogeneous catalysis is not being applied as widely as it should be in practice and is not being investigated very thoroughly from either the theoretical and experimental standpoint. This observation refers particularly to homogeneous catalysis of gas reactions. Nevertheless, research on problems of homogeneous catalysis, especially as applied to reactions following a mechanism of the chain type, offers wide possibilities for the clarification of the catalytic mechanism (the role of the catalyst in the initiation, growth, and branching of the chain), as well as for the establishment of effective ways for the practical use of homogeneous catalysts.

In connection with the considerable interest attached in contemporary chemical kinetics to the problem of the oxidation of hydrocarbons, we deemed it relevant to concentrate our attention on the systematic study of homogeneous catalysis in the processes involved. In a preceding report [1] we reviewed the action of various homogeneous additives to propane on the oxidation reaction, showing that already a preliminary knowledge of the action of various catalysts permits to outline a tentative direction for further investigations.

This report discusses the results of studying the kinetics of the oxidation of propane in the presence of HBr, which is a specific and highly effective homogeneous catalyst permitting direction of the oxidation process toward the side of acetone formation [2].

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The reaction of an equimolecular mixture of propane and oxygen containing 3 to 20% HBr was studied in a closed reaction vessel made of ordinary glass through the temperature interval of 168-216° at pressures between 50-550 mm of mercury. Below 168° the reaction proceeds slowly and leads to a low yield of acetone. Above 216° and especially with high amounts of HBr, the reaction mixture bursts into flame.

The yield of acetone increases as the temperature is raised (within the stated temperature interval) and as the content of HBr in the mixture is raised. The yield also depends on the condition of the walls of the reaction vessel. The maximum yields of acetone, large in themselves, never exceed ~50% in relation to the original propane. In the course of the process, hydrogen bromide is consumed in irregular and sometimes considerable quantities (depending on the condition of the walls of the reaction vessel). There is no connection between the yield of acetone and the consumption of HBr. A peculiarity of the kinetic curve of HBr consumption is that the catalyst ceases to be spent long before the cessation of the process of acetone formation. The process of the formation of acetone and the consumption of HBr with the formation of bromorganic compounds are parallel reactions that are not connected with each other. Furthermore, in the course of the reaction, noticeable quantities (10-15% of the yield of acetone) of organic acids (acetic and propionic) form, as well as an organic hydroperoxide (approximately 2.5% of the original propane). The change in concentration of each component during the course of the reaction is shown in our previous report [1].

In Figure 1 (appended) is shown a sequence of kinetic curves for the formation of acetone at various temperatures from 168 to 216° for a mixture (at 80 mm of Hg) of $C_3H_8 + 80 \text{ mm } O_2 + 17 \text{ mm HBr}$. The increases in the speed and the extent of the reaction as the temperature is increased are seen clearly. The simple type of the kinetic curves for the end product of the reaction in a complex three component system attracts attention. The kinetic curves in Figure 1 are well described by the equation for the monomolecular reaction

$$(CH_3COCH_3) = (CH_3COCH_3)_\infty (1 - e^{-kt}), \quad (1)$$

the only difference being that instead of using the starting concentration of any of the original components as a yardstick for complete conversion, the quantity of the end product at the completion of the process $(CH_3COCH_3)_\infty$ is used.

The rate constant for the reaction is

$$k = 2 \cdot 10^9 \cdot e^{-25000/RT}. \quad (2)$$

Subsequent experiments showed that the monomolecularity of the reaction is conserved with changes in composition of the starting mixture over a wide interval. Only the extent of the reaction is altered, i.e., the final yield of acetone $(CH_3COCH_3)_\infty$. This means that in the event that the experiments are carried out at a constant temperature but with varying quantities of starting materials, all of the kinetic curves must merge into one after the scale for the extent of the conversion has been altered.

The result of this conversion is shown in Figure 2. The caption states the composition of the mixtures for which the kinetic curves were drawn.

The simplest explanation of the monomolecular rule could be as follows: As a result of the first rapid stage, an intermediate product forms, which then (second stage) slowly decomposes by the monomolecular rule to form acetone. This scheme requires that at the first moment of the reaction a considerable

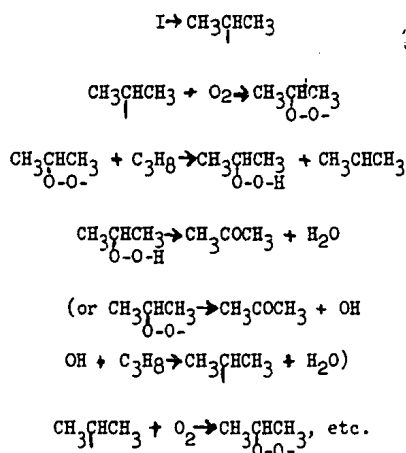
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part of the propane and oxygen (corresponding to the final yield of acetone) should convert into the intermediate product. Experimentally, however, an extensive conversion of the initial substances is not observed in the early stages of the reaction. For this reason we assume that the process of the formation of acetone comprises two stages, both of which proceed by a chain mechanism. After the first rapid and self-stopping reaction, a small amount of the intermediate catalyst $(I)_0$ is formed. A chain reaction with branched chains could serve as a model for such a process. The existence of limits for the speed of the process is typical for this kind of reaction.

In the second stage, the intermediate catalyst I now decomposes slowly by the monomolecular rule, inducing by every act of the decomposition an unbranched chain reaction of the formation of acetone, as shown on the example given in the following scheme:



In this manner, small amounts of the intermediate catalyst, decomposing in the course of the process, are multiplied into the long chain of the reaction leading to the formation of acetone.

The proposed mechanism leads in a simple manner to the monomolecular rule for the formation of acetone. The intermediate product decomposes monomolecularly

$$(I) = (I)_0 e^{-kt}. \quad (3)$$

During the interval of time t , an amount of intermediate catalyst decomposes which is equal to

$$(I)_0 - (I) = (I)_0 (1 - e^{-kt}). \quad (4)$$

Inasmuch as every act of the decomposition of a molecule of the intermediate catalyst initiates a reaction chain leading to the formation of ν molecules of acetone, the amount of acetone formed at this moment (at the expiration of the time t) will be

$$(\text{CH}_3\text{COCH}_3) = \nu [(I)_0 - (I)] = \nu (I)_0 (1 - e^{-kt}). \quad (5)$$

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This is the rule (1) already noted by us, where

$$(\text{CH}_3\text{COCH}_3) = (I)_c. \quad (6)$$

This conclusion applies strictly under the conditions that the initiating reaction is practically instantaneous and that the concentration of the intermediate catalyst reaches its limiting value near the beginning of the process, i.e., in the vicinity of $t = 0$.

Later on we shall demonstrate that a certain time is required in order for the initiating reaction to take place. Therefore, the rate of acetone formation is greatest not at $t = 0$, but at the moment of time t corresponding to the end of the initiating reaction, i.e., to the maximum concentration of the intermediate catalyst. In other words, at the starting moment of the reaction the phenomenon of autoacceleration should be observed if a precise analysis of the process is made. This initial acceleration should be the more pronounced the longer the initiating reaction. The kinetic curves given in the present report do not exhibit an initial acceleration, i.e., the initiating reaction occurs rapidly under the conditions studied.

It is very probable that not only the extent but also the duration of the initiating reaction depends on the condition of the reaction vessel. This means that by applying proper surface treatment, it ought to be possible to obtain kinetic curves of various types - beginning with the curve for the monomolecular reaction and passing on to curves with various initial accelerations.

[See figures on following page.]

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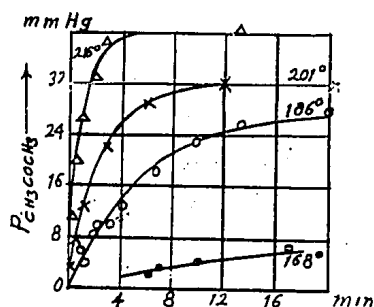


Figure 1. Kinetic curves for the formation of acetone in a mixture of propane, oxygen, and HBr at various temperatures

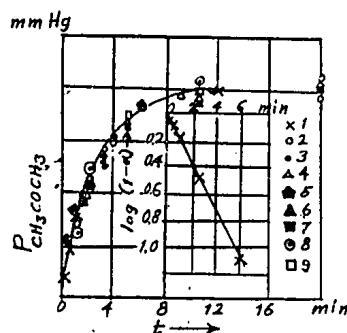


Figure 2. Congruency of kinetic curves for the formation of acetone, taken at 201° for mixtures with various ratios of C_3H_8 , O_2 , and HBr.

- 1 - 80 mm C_3H_8 + 80 mm O_2 + 17 mm HBr;
- 2 - 80 mm C_3H_8 + 64 mm O_2 + 16 mm N_2 + 17 mm HBr, $(CH_3COCH_3)_\infty = 28$ mm;
- 3 - 80 mm C_3H_8 + 43 mm O_2 + 37 mm N_2 + 17 mm HBr, $(CH_3COCH_3)_\infty = 22$ mm;
- 4 - 80 mm C_3H_8 + 22 mm O_2 + 58 mm N_2 + 17 mm HBr, $(CH_3COCH_3)_\infty = 15$ mm;
- 5 - 80 mm C_3H_8 + 80 mm O_2 + 26 mm HBr, $(CH_3COCH_3)_\infty = 37$ mm;
- 6 - 80 mm C_3H_8 + 80 mm O_2 + 13 mm HBr, $(CH_3COCH_3)_\infty = 20$ mm;
- 7 - 80 mm C_3H_8 + 80 mm O_2 + 8 mm HBr, $(CH_3COCH_3)_\infty = 12$ mm;
- 8 - 64 mm C_3H_8 + 80 mm O_2 + 16 mm N_2 + 17 mm HBr, $(CH_3COCH_3)_\infty = 27$ mm;
- 9 - 43 mm C_3H_8 + 80 mm O_2 + 37 mm N_2 + 17 mm HBr, $(CH_3COCH_3)_\infty = 16$ mm.

On the same figure the kinetic curve is also drawn in the coordinates $\sqrt{1-a}$, where

$$a = \frac{(CH_3COCH_3)}{(CH_3COCH_3)_\infty}$$

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